

Appl. No. 09/891/272  
Amdt. Dated 11/21/03  
Reply to Office action of July 24, 2003

**REMARKS/ARGUMENTS**

Thank you for your telephone conversation on November 5, 2003. You had reviewed the draft of my reply to the Office Action of July 24, 2003 which I faxed to you on October 28. You indicated that the reply seemed to be in order. You added, however, that it would be helpful to have some additional information about the difference between the preparation of magnetite in the Molday procedure and the preparation of magnetite in my procedure. In particular, you asked for information about why the presence or absence of dextran during the precipitation of magnetite is important. I have added an explanation in my response to the Examiner's rejection of claims as being anticipated by Molday (US 4,452,773). I hope this clarifies the issue.

In the specification, paragraph [0087] has been amended to clarify the significance of "60 nm", which is the standard deviation about the average diameter rather than the range of diameters.

The wording that appeared in claim 1, line 6, has been changed from "formed of a particle" to "comprising an aggregate" in order to provide better clarity as to the nature of the magnetizable particle of applicant's invention.

The term "aggregate of crystallites" has been used to replace the phrase "particles of crystallites" in claim 1 and dependent claims to avoid the confusion arising from the use of the term "particles" to refer to both aggregates of crystallites and entire magnetizable particles.

The term "aggregate of crystallites" has been used in claim 1 and the dependent claims to better distinguish the nature of the magnetizable particles of the present invention from those taught by Molday (US 4,452,773).

The term "magnetizable particle comprising an aggregate" is intended to include both a magnetizable particle with a single aggregate and a magnetizable particle with more than one aggregate.

In claim 1 and dependent claims, the phrase "liquid mixture" has been substituted for the term "suspension or dispersion". The term "mixture" is used repeatedly in the specification (see, for example, paragraph [0021], lines 2 and 3), and the phrase "liquid mixture" is clearer and simpler than the phrase "suspension or dispersion". The phrase "a mass of" adds no clarity and is thus unnecessary and has been removed. The phrase "combining with" is in more

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common usage than the phrase "combining to", has substantially the same meaning, and thus is preferred and has been substituted.

In claims 4 and 5, the term "magnetic" was used in error and has been replaced with the term "magnetizable", which is used consistently elsewhere in the claims, to provide proper antecedence.

In claims 11 and 12, the term "precipitated magnetite" is substituted for the term "magnetizable aggregates" to avoid confusion with the term "aggregate of crystallites" and to more clearly specify the actual material being used.

Claims 1-19 remain in this application. Claims 1,3-7, 10-12, and 14 are currently amended. Claims 2, 8, 9, 13, 15-19 are original. Claim 53 is new. Claims 20-52 are withdrawn.

**Response to Rejection of Claims 1-19, 52 under 35 U.S.C. 112.:**

Applicant thanks the examiner for pointing out the confusing wording with respect to the attachment of the coupling group in claim 1. Applicant has amended claim 1 to provide greater clarity. The phrase "which coupling group is attached by means of said functional group to said polysaccharide coating" has been added to make clear the means of attaching the coupling group to the magnetizable particle.

Applicant thanks the examiner for pointing out that claim 14 is unclear. The phrase "such as halide or sulfonate" was intended to be exemplary, not limiting, and the phrase has been removed in the amended claim.

Applicant kindly requests that the rejection under 35 U.S.C. 112 be withdrawn in view of the above amendments to claims 1 and 14.

**Response to Rejection of Claims 1, 2, 4, 5, 9, 11, 14, 19 under 35 U.S.C 102(b) as being anticipated by Molday (US 4,452,773):**

Examiner has predicated rejection of the above-cited claims on the basis that Molday teaches a method that is identical to the method given in Example 1 of the specification of the present invention. On page 4, lines 5-6 of the Office

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Action, it is stated "Molday teaches the same method of making particles as in Example 1 of the specification of the present invention." This statement is not correct. Molday teaches a method in which the ferrous and ferric salts are mixed with a coating material such as dextran before being added to the base, and therefore the magnetite ( $Fe_3O_4$ ) is precipitated in the presence of this coating material (see Molday, column 8, lines 34-40). In Example 1 of the specification of the present invention, the ferrous and ferric salts are not mixed with any coating material, and thus the magnetite is precipitated in the complete absence of any coating material (see paragraph [0078], lines 1-3, and paragraph [0079], lines 1-5).

The presence (as in Molday) or absence (as in the present invention) of dextran during the precipitation of magnetite profoundly affects the course of the precipitation. In the absence of dextran, there is no coating on the crystallite. Therefore, the crystallites can directly contact one another to form aggregates. In the appended paper by Jolivet and Tronc, in which the authors prepare magnetite in a manner similar to that used in the present invention, the authors refer to the initially prepared magnetite as a solid (pg 689, lines 5 and 8) and note that it is somewhat difficult to prepare a uniform suspension of this solid (lines 15-16). Furthermore, they state that without additional treatment of this precipitated magnetite, a colloid cannot be prepared (see pg 699, column 2, last paragraph, and pg 700, column 1, third paragraph).

In Molday's invention, magnetite is precipitated in the presence of dextran. The particles of his invention are produced directly in his reaction mixture, with no additional treatment steps. Each crystallite is coated with dextran. Molday states (column 3, line 16) that his particles do not aggregate. Thus it is not possible to form aggregates of crystallites by following the teaching of Molday. The formation of an aggregate of crystallites is an important part of the present invention. Not only is Molday's procedure different from that used in the present invention, but it also results in crystallites of magnetite which will not aggregate, and are thus totally unsuited for use in the present invention.

Because the method of making the magnetizable particles used in applicant's invention is different and distinct from the method of making particles taught by Molday, the particles themselves are not identical, and in fact are different and distinct. Among the differences are the following:

*The nature of the core.* Molday teaches the preparation and use of a particle with an electron dense core of 10-20 nm. The size of this core is consistent with the size of a single crystallite of magnetite prepared by

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precipitation of mixed iron salts with ammonia, as noted in the appended paper by Jolivet and Tronc (see pg 690, column 2, line 7, where a particular preparation had an average crystallite diameter of 9 nm). Further, Molday makes no comment about the presence of multiple objects in the electron dense core of his particle, and hence we may presume that the core is a single object, a single crystallite. Thus applicant's particles, which have as their core an aggregate of crystallites, are different and distinct from Molday's particles which have a single crystallite as their core.

*The nature of the mineral in the core.* Molday is very specific in his teaching that the iron oxide in the core of the particle which he prepares and uses is Fe<sub>3</sub>O<sub>4</sub>. The iron oxide in the core of the particles of the present invention is not Fe<sub>3</sub>O<sub>4</sub>. The appended paper by Jolivet and Tronc attests to the fact that the method by which applicant prepares the colloidal aggregates of magnetizable iron oxide transforms the initially prepared magnetite into a different iron oxide (see pg 688, column 2, lines 8-12, and pg 699, column 1, lines 19-23). This paper also states that unless this transformation occurs, a colloid cannot be prepared (see pg 699, column 2, last paragraph).

*The size of the magnetizable particle.* Molday teaches the preparation and use of a particle with a diameter of 10-70 nm, and more usually 30-40 nm (column 3, lines 19-20), whereas the particles of the applicant's invention are much larger (for example, see one non-limiting embodiment in paragraph [0087], lines 13-14, of the inventor's application where the preparation of magnetizable particles of average diameter of 190 nm is described.)

For the above cited reasons, applicant respectfully submits that the particles of applicant's invention are not identical to the particles taught by Molday, and that Molday does not anticipate the applicant's invention.

Applicant kindly requests that the rejection of claims 1, 2, 4, 5, 9, 11, 14, 19 under 35 U.S.C 102(b) be withdrawn.

**Response to Rejection of Claims 3, 6-8, and 52 under 35 U.S.C. 103(a) as being unpatentable over Molday (US 4,452,773) further in view of Chagnon, et. al. (US 4,628,037).**

As discussed above, Molday does not teach the magnetizable particles of the present invention. Chagnon does not teach the magnetizable particles of the

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present invention. Therefore Chagnon and Molday in combination do not teach the magnetizable particles of the present invention.

Applicant kindly requests that the rejection of claims 3, and 6-8, under 35 U.S.C. 103(a) be withdrawn.

**Response to Rejection of Claims 15-17 under 35 U.S.C. 103(a) as being unpatentable over Molday (US 4,452,773) further in view of Niswender (US 4,048,298).**

As discussed above, Molday does not teach the magnetizable particles of the present invention. Niswender does not teach the magnetizable particles of the present invention. Therefore Niswender and Molday in combination do not teach the magnetizable particles of the present invention.

Applicant kindly requests that the rejection of claims 15-17 under 35 U.S.C. 103(a) be withdrawn.

In view of the examiner's restriction requirement, applicant retains the right to present claims 20-51 in a divisional application.

Applicant respectfully requests that a timely Notice of Allowance be issued in this case.

Please notify me either by telephone or by e-mail when this reply reaches your desk. I will be happy to provide further clarification if it is needed.

Respectfully submitted,



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## Interfacial Electron Transfer in Colloidal Spinel Iron Oxide. Conversion of $\text{Fe}_3\text{O}_4$ - $\gamma\text{Fe}_2\text{O}_3$ in Aqueous Medium

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The behaviour of colloidal  $\text{Fe}_3\text{O}_4$  ( $\sim 100 \text{ \AA}$ ) in weakly acidic medium (pH 2–2.5) has been investigated by potentiometry, X-ray diffraction, and Mössbauer spectroscopy. Complete and exclusive removal of FeII without noticeable particle size effect is reported. Subsequent  $\text{Fe}_3\text{O}_4 \rightarrow \gamma\text{Fe}_2\text{O}_3$  transformation is suggested to proceed with selective surface leaching of FeII ions reduced by electron core-to-surface transfer. An analogous conversion is experienced in the presence of FeIII in solution, but it is characterized by significant structural disordering in the surface. © 1988 Academic Press, Inc.

### INTRODUCTION

Phenomena at the interface between metal oxides and electrolyte solutions play an important role in various areas such as metal corrosion, plant decontamination, heterogeneous catalysis, or soil chemistry. Many studies deal with iron oxides, and particularly the spinel ones (magnetite  $\text{Fe}_3\text{O}_4$ , maghemite  $\gamma\text{Fe}_2\text{O}_3$ ).

Studies on magnetite mainly focus either on the oxide dissolution (1–4) or on metal adsorption (5–8). In the former case, the goal is the lattice destruction, and drastic conditions are therefore used (strongly acidic and/or complexing medium, reducing or oxidizing agent, high temperature). In the latter case, adsorption of metallic cations, generally hydrolyzable, is of concern: mild conditions, in very weakly acidic medium (pH 4–5), are required. Then chemical reactions are limited at the oxide surface, and they do not involve the underlying lattice. Interfacial properties of large  $\text{Fe}_3\text{O}_4$  particles ( $0.1$ – $10 \mu\text{m}$ ) are thus well described using classical site binding models (9, 10). It has, however, been reported that in weakly acidic medium (pH 2–4)  $\text{Fe}_3\text{O}_4$  slightly releases FeII (ca. a few percent) (11). On the

other hand, natural magnetite samples (12), deslimed with concentrated HCl, exhibit anomalous magnitude and dependence of the positive surface charge compared to other oxides.

With decreasing particle size, surface phenomena are enhanced and particular features may occur. Thus, colloidal particles of magnetite, about  $100 \text{ \AA}$  in size, lead to stable sols in acidic medium (13) but, simultaneously, they release FeII ions, finally giving particles with composition close to  $\text{Fe}_2\text{O}_3$ . Increasing the pH can make these particles readsorb all released FeII (14): a magnetite layer grows epitaxially at the surface, whereas FeIII ions in the octahedral sublattice in the interior are likely reduced. The reaction was suggested to be assisted by an electron transfer through the interface into the particle.

Here, we report results on the behaviour of colloidal magnetite in weakly acidic medium (pH 2–2.5), in various experimental conditions. The aim is a better understanding of the phenomena which induce the transformation  $\text{Fe}_3\text{O}_4$ - $\gamma\text{Fe}_2\text{O}_3$  without an oxidizing agent, and which enable surface charge to develop on the particle to give stable sols.

Aerial oxidation of magnetite has been

widely investigated (15–19).  $\text{Fe}_3\text{O}_4$  particles stirred in aqueous medium are transformed into  $\gamma\text{Fe}_2\text{O}_3$  at about 200°C. At room temperature, oxidation occurs spontaneously and produces materials with a unit cell parameter (8.36 Å) in between that of  $\text{Fe}_3\text{O}_4$  (8.40 Å) and  $\gamma\text{Fe}_2\text{O}_3$  (8.33 Å). This is generally attributed to lattice defects, protons, or hydroxyl groups rather than to FeII ions still present in the structure. Structural refinement (20) has shown that the presence of iron in interstitial tetrahedral sites is the salient feature. This disordered structure can probably accommodate a large amount of FeII and/or hydrogen; it does not differ much from the  $\gamma\text{Fe}_2\text{O}_3$  structure which it will be assimilated to, below, for the sake of simplicity.

We recall that  $\text{Fe}_3\text{O}_4$  is an inverse spinel. Oxygen ions make a cfc stacking. FeIII ions equally occupy tetrahedral (A) and octahedral (B) sites. FeII ions are localized on sublattice B. The unit cell content may be written as  $(\text{Fe}_8^{III})_A(\text{Fe}_8^{III}\text{Fe}_8^{II})_B\text{O}_{32}$ . At room temperature, a fast electron hopping ( $\sim 10^{-10}$  sec) (21) occurs between FeII and FeIII ions of type B.  $\gamma\text{Fe}_2\text{O}_3$  is a deficient spinel, with vacancies

localized on sublattice B. In the absence of vacancy ordering, the unit cell remains cubic, and its content may be written as  $(\text{Fe}_8^{III})_A(\text{Fe}_{40/3}^{III}\square_{8/3})_B\text{O}_{32}$ , where  $\square$  represents a vacancy. Incorporation of protons or alkali ions in sublattice B has been postulated (19) as paralleling the structure  $\text{LiFe}_5\text{O}_8$ . However, the presence of these or other ions in materials made by the precipitation method seems likely related to specific adsorption and surface charge phenomena (13, 22).

## EXPERIMENTAL

### SYNTHESIS

Colloidal magnetite was prepared by alkalinizing aqueous FeII and FeIII ions. The stoichiometric mixture  $\text{FeII} + 2\text{FeIII}$  ( $10 \text{ cm}^3 \text{FeCl}_2 \text{ moles} \cdot \text{dm}^{-3}$ ,  $\text{HCl} 2 \text{ moles} \cdot \text{dm}^{-3} + 40 \text{ cm}^3 \text{FeCl}_3 1 \text{ mole} \cdot \text{dm}^{-3}$ ) was slowly added to a  $\text{NH}_3$  solution ( $400 \text{ cm}^3, 0.9 \text{ mole} \cdot \text{dm}^{-3}$ ) and

vigorously stirred. Great care was taken to exclude oxygen during all the stages of the preparation. All solutions were carefully deaerated with nitrogen, which was continuously bubbled during the reaction. The solid was separated by magnetic settling, the supernatant being eliminated under  $\text{N}_2$  pressure. The solid was washed in the reaction flask with degassed distilled water introduced under  $\text{N}_2$  pressure, and separated again. This was repeated twice. The colloid was then dispersed in deaerated distilled water and kept in an argon atmosphere. The pH was ca. 8.5, and the total concentration in Fe was ca. 0.5  $\text{mole} \cdot \text{dm}^{-3}$ . After prolonged stirring, suspension samples could be taken reproducibly.

Colloidal cobalt ferrite ( $\text{Fe}_2\text{CoO}_4$ ) was prepared by adding the mixture  $\text{Co}(\text{NO}_3)_2 + 2\text{FeCl}_3$  to a  $\text{NaOH}$  solution with vigorous stirring at 90°C. The solid was separated by magnetic settling, washed twice with distilled water, and dispersed in distilled water to give a suspension whose concentration in Fe was approximately 0.3  $\text{mole} \cdot \text{dm}^{-3}$ .

## TECHNIQUES

The suspension composition was determined after dissolving the colloid into concentrated HCl. Fe titration was determined by atomic absorption spectrophotometry (Perkin-Elmer Type 373) or by potentiometry. FeII was titrated using  $\text{K}_2\text{Cr}_2\text{O}_7$  in HCl (6  $\text{moles} \cdot \text{dm}^{-3}$ ). At the titration end, total Fe was reduced by a  $\text{SnCl}_2$  solution and the solution was titrated again with  $\text{K}_2\text{Cr}_2\text{O}_7$  (23), which gave the total Fe content. Co was titrated by atomic absorption spectrophotometry or by potentiometry using a base.

For protometric titrations, an aliquot of suspension homogenized by stirring was poured into  $20 \text{ cm}^3$  of deaerated water, along with a varying volume of  $\text{HClO}_4$  (0.2  $\text{mole} \cdot \text{dm}^{-3}$ ) or of  $\text{Fe}(\text{NO}_3)_3$  (0.1  $\text{mole} \cdot \text{dm}^{-3}$ ).  $\text{N}_2$  was continuously bubbled and titration was performed by adding  $\text{N}(\text{CH}_3)_4\text{OH}$  ( $1 \text{ cm}^3 \cdot \text{min}^{-1}$ ) using a potentiograph Metrohm E 536.

Kinetics studies were performed by taking samples in the course of the reaction, and by titrating with  $\text{N}(\text{CH}_3)_4\text{OH}$ . With  $\text{HClO}_4$  as a reagent, the starting molar ratio  $|\text{H}^+|/|\text{FeII}|$  was fixed at 2, and acid concentration was initially  $5 \times 10^{-2}$  mole  $\cdot$  dm $^{-3}$ . In the case of  $\text{Fe}(\text{NO}_3)_3$ , the reaction mixture corresponded to  $|\text{FeIII}|/|\text{FeII}| = 0.66$ , and the initial concentration of  $\text{FeIII}$  added was  $5 \times 10^{-2}$  mole  $\cdot$  dm $^{-3}$ .

Transmission electron micrographs were obtained using a Jeol 100 CXII apparatus. Samples were prepared by evaporating very dilute sols or suspensions onto a carbon-coated grid. Particle size distributions were estimated by measuring 200 to 500 particles.

X-ray diffraction (XRD) and Mössbauer effect investigations were performed on solids. In order to prevent  $\text{Fe}_3\text{O}_4$  from drying-induced oxidation, the Mössbauer sample was prepared by dispersing a fraction of suspension into an aqueous solution of polyvinyl alcohol (20 g/100 cm $^3$  H $_2$ O), and by drying the mixture under N $_2$  circulation. It gave a rigid homogeneous film. For XRD study, a fraction of suspension was centrifuged, and the solid was packed in the sample holder and protected in front with a thin varnish coating. For oxidized materials, a fraction of suspension or of sol was ultrafiltered using a cell Amicon (membrane P30). The solid was washed with water, ultrafiltered again, and dried under reduced pressure. Powders were dispersed in an acrylic resin (Presi Mecaprex) for Mössbauer sampling.

Mössbauer spectra were recorded at room temperature using a conventional spectrometer (Elscint-Inel) and a  $^{57}\text{Co}/\text{Rh}$  source. Velocities were calibrated using an iron foil. Absorbers had an effective thickness in the range 5–10 mg Fe/cm $^2$ .

XRD measurements were performed using a powder diffractometer (Philips PW 1380) operating in the reflection mode with  $\text{CoK}_\alpha$  radiation at a scanning rate of  $0.25^\circ 2\theta \text{ min}^{-1}$ . Line widths ( $X$ ) were evaluated from the widths at half maximum assuming Gaussian profiles for intrinsic and experimental broadenings. Integrated intensities were collected up

to the line 440, corrected for background, and for Lorentz and polarization effects calculated at peak maximum positions.

## RESULTS

Freshly prepared magnetite was characterized by a ratio  $|\text{FeII}|/|\text{FeIII}|$  always in the range 0.47–0.50. The particles, roughly spherical, were of ca. 90 Å in size ( $\sigma \sim 25$  Å).

### 1. CHEMICAL STUDY

#### 1.1. Behaviour in Acidic Medium

Acidifying the suspension with  $\text{HClO}_4$  to pH 2–2.5 caused  $\text{FeII}$  ions, with exclusion of  $\text{FeIII}$ , to be released immediately into solution.

The titration curve of the solution separated by ultrafiltration is given in Fig. 1. It shows two equivalent points, roughly at pH 5 (A) and pH 9 (B), separated by a step at pH 8 corresponding to precipitation of  $\text{Fe}(\text{OH})_2$ . Point A marks the end of the neutralization of excess free acidity and of  $\text{FeIII}$  ions if present in the solution. Because the amount of  $\text{FeII}$  neutralized between A and B is exactly equal to the Fe amount deduced from the atomic

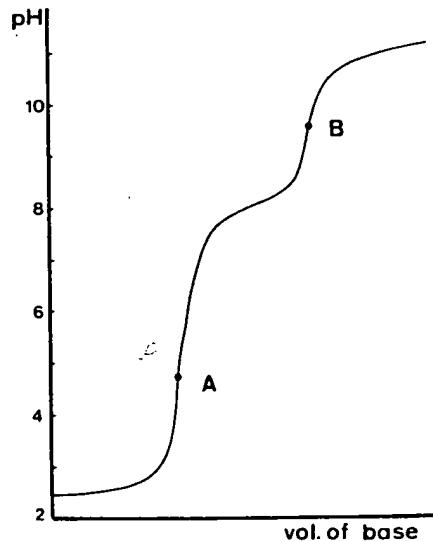


FIG. 1. Titration by  $\text{N}(\text{CH}_3)_4\text{OH}$  of the ultrafiltrate of a mixture of  $\text{Fe}_3\text{O}_4 + \text{HClO}_4$  ( $|\text{H}^+|_{\text{ad}}/|\text{Fe}| = 0.24$ ).

absorption analysis, it was deduced that Fe was exclusively in the FeII state in the filtrate, and point A corresponded to neutralization of excess free acidity only.

Titration curves of the suspension variously acidified prior to titration are given in Fig. 2. The step associated with precipitation of  $\text{Fe}(\text{OH})_2$  is shifted down to ca. pH 6, owing to the colloid presence. In the experimental conditions, as  $\text{Fe}(\text{OH})_2$  forms up, it is actually adsorbed on the colloid surface (14). That alters the precipitation pH, but not the reaction stoichiometry, and the concentration of free species ( $\text{H}^+$ , FeII) can still be assessed straight from the titration.

Neutralization of the overall system ends at pH 8.6. The total amount of base needed plotted against the amount of acid added prior to titration gives a straight line of slope 1 (Fig. 3a). The amount of released FeII ions ( $|\text{FeII}|_R$ ) plotted against the amount of consumed protons ( $|\text{H}^+|_c$ ), not neutralizable at pH 4.5, yields a straight line of slope 0.5 (Fig. 3b). Hence, it is deduced that two protons are consumed when one FeII ion is released into solution.

The reaction kinetics is given in Fig. 4. It clearly exhibits two distinct stages. The first one corresponds to quasi-instantaneous desorption of ca. 40% of the colloid FeII ions. The second one, very slow, corresponds to desorption of remaining FeII ions. After 100 hr, 80% of FeII ions were released. After a month, roughly 1% still remained in the colloid. The process of FeII desorption can be accelerated by increasing the acid concentration, but then the particles get eroded significantly and FeIII appears in solution. In the experimental conditions we used, the reaction stoichiometry was always conserved. The ratio  $|\text{H}^+|_c/|\text{FeII}|_R$  remained near 2 all along the reaction, and FeIII ions were never detected in solution.

Moreover, as soon as the concentration ratio  $|\text{FeII}|/|\text{FeIII}|$  in the particle was lowered to ca. 0.15, peptization occurred, giving homogeneous sols. At completion of FeII desorption ( $|\text{FeII}|/|\text{FeIII}| \sim 0.01$ ), the colloid was ultrafiltered and redispersed in water. The positive surface electric charge was evaluated by titrating with  $\text{N}(\text{CH}_3)_4\text{OH}$ . The charge measured as the ratio of titratable  $\text{H}^+$  over the Fe content was of the order of 0.01, giving a sur-

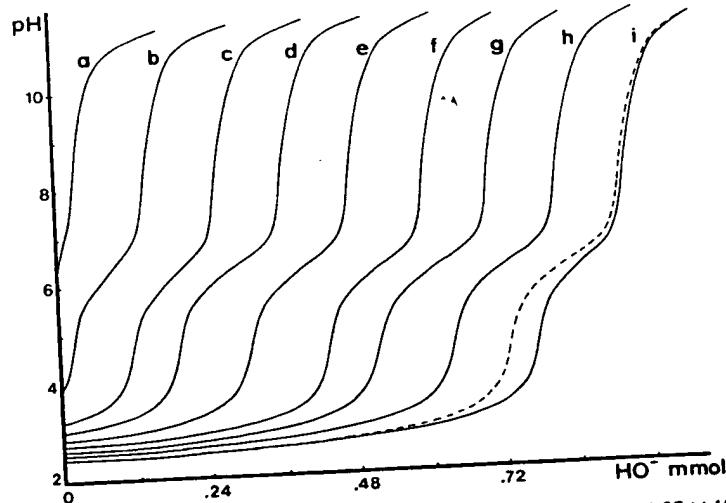


FIG. 2. Titration of mixtures  $\text{Fe}_3\text{O}_4 + \text{HClO}_4$ .  $1.18 \times 10^{-3}$  mole Fe,  $|\text{Fe}|_{\text{total}} = 4.37 \times 10^{-2}$  mole  $\cdot \text{dm}^{-3}$ , and  $|\text{H}^+|_{\text{ad}}/|\text{Fe}| = x$ .  $x = 0$  (curve a); 0.1 (b); 0.19 (c); 0.30 (d); 0.39 (e); 0.49 (f); 0.59 (g); 0.69 (h); 0.79 (i). Titrations were performed 5 min (45 min for dashed line in (i)) after acid addition, using  $\text{N}(\text{CH}_3)_4\text{OH}$  ( $0.24 \text{ mole} \cdot \text{dm}^{-3}$ ) added at the rate of  $1 \text{ cm}^3 \cdot \text{min}^{-1}$ .

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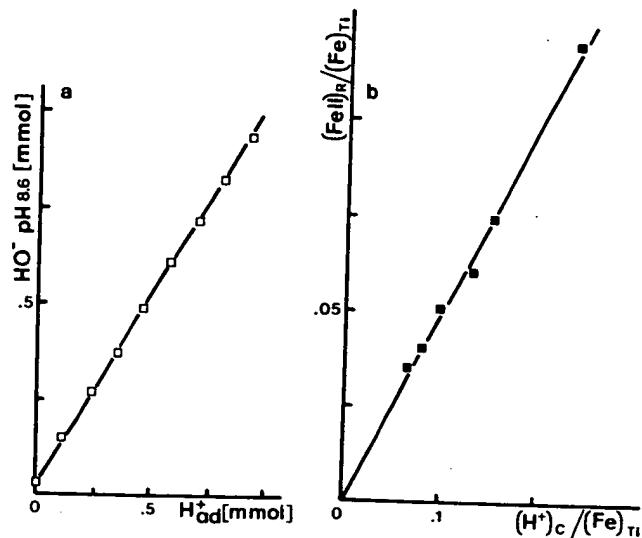


FIG. 3. Exploitation of titration of mixtures  $\text{Fe}_3\text{O}_4 + \text{HClO}_4$ . Data deduced from curves given in Fig. 2. (a) Amount of base added at pH 8.6 vs amount of acid initially added ( $\text{H}^+_{\text{ad}}$ ). (b) Amount of released  $\text{Fe}^{II}$  ( $|\text{Fe}^{II}|_R$ ) vs amount of consumed protons (not titratable at pH 4.5) ( $|\text{H}^+|_c$ ). Amounts are relative to total Fe initially in  $\text{Fe}_3\text{O}_4$  ( $|\text{Fe}|_{Ti}$ ).

face charge of  $10 \mu\text{C}/\text{cm}^2$  (assuming 100-Å particles). It compares well with data obtained for similar colloids in stronger acidity conditions (13).

Comparison of electron micrographs of magnetite before and after the treatment with acid indicates no significant alteration of the

particle size (Table I). These results therefore show that mild acidification of colloidal  $\text{Fe}_3\text{O}_4$  induces a quantitative net "exchange" between  $\text{Fe}^{II}$  ions in the solid and protons in the solution ( $\text{Fe}^{II}/2\text{H}^+$ ), without a noticeable size effect, and that it results in the particle peptization.

### 1.2. Behaviour in $\text{Fe}^{III}$ Medium

Release of  $\text{Fe}^{II}$  ions was also observed for colloidal  $\text{Fe}_3\text{O}_4$  in the presence of  $\text{Fe}(\text{NO}_3)_3$ .

TABLE I

Sample Characteristics

Sample*	$\text{Fe}^{II}/\text{Fe}^{III}$	$D_0^b$ (Å)	$\bar{D}$ (Å)	$\sigma$ (Å)
M	0.48	74	84	21
O	0.10		Not determined	
H	0.07	74	81	18
Fe	0.05	80	85	15

\* Sample labelling is: magnetite freshly prepared (M), treated with  $\text{HClO}_4$  (H), treated with  $\text{Fe}(\text{NO}_3)_3$  (Fe), and dried and aged in air (O).

<sup>b</sup>  $D_0$  is the most probable diameter in the particle size distribution,  $\bar{D}$  is the mean diameter, and  $\sigma$  is the standard deviation.

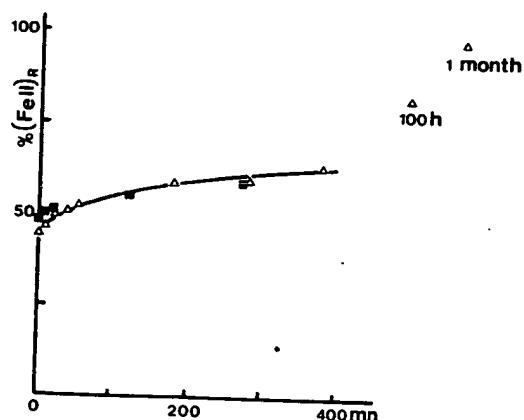


FIG. 4. Kinetics of release of  $\text{Fe}^{II}$  ( $|\text{Fe}^{II}|$ ) in mixtures of  $\text{Fe}_3\text{O}_4 + \text{HClO}_4$  ( $\Delta$ ) and  $\text{Fe}_3\text{O}_4 + \text{Fe}(\text{NO}_3)_3$  ( $\blacksquare$ ) at  $25^\circ\text{C}$ . ( $\Delta$ )  $4.04 \times 10^{-3}$  mole  $\text{Fe}_3\text{O}_4$ ;  $|\text{H}^+|_{\text{init}} = 5 \times 10^{-2}$  mole  $\cdot \text{dm}^{-3}$ ;  $|\text{H}^+|_{\text{ad}}/|\text{Fe}^{II}|_{\text{init}} = 2$ . ( $\blacksquare$ )  $7.5 \times 10^{-3}$  mole  $\text{Fe}_3\text{O}_4$ ;  $|\text{Fe}^{III}|_{\text{ad}} = 5 \times 10^{-2}$  mole  $\cdot \text{dm}^{-3}$ ;  $|\text{Fe}^{III}|_{\text{ad}}/|\text{Fe}^{II}|_{\text{init}} = 0.66$ .

Owing to acidity of FeIII ions, the initial pH of the mixture was similar to that in Section I... Potentiometric titration and atomic absorption analysis of the filtrate of ultrafiltered mixtures gave evidence of Fe in solution in the FeII and in the FeIII state, and of FeIII consumption.

Titrating the suspension in the presence of a varying quantity of  $\text{Fe}(\text{NO}_3)_3$  previously added led to curves shaped similarly to those in Fig. 2, with equivalent points at pH 3.5-4 and pH 8.5. The amount of FeIII consumed by the particles ( $|\text{FeIII}|_c$ ) was deduced by subtracting the amount of FeIII precipitated as  $\text{Fe}(\text{OH})_3$  at pH 3.5-4 from the amount of FeII added prior to titration ( $|\text{FeIII}|_{ad}$ ). The amount of FeII released into solution ( $|\text{FeII}|_R$ ) was evaluated from the quantity of base added between the two equivalent points. The total amount of base added up to pH 8.5 plotted against  $|\text{FeIII}|_{ad}$  (Fig. 5a) yields a straight line of slope 3. The plot  $|\text{FeII}|_R$  versus  $|\text{FeIII}|_c$  (Fig. 5b) gives a straight line of slope 1.5.

Hence, the net reaction is the substitution of two FeIII ions by three FeII ions in solution.

Reaction kinetics and peptization features were similar to those observed in acidic medium.

### 1.3. Behaviour of Colloidal $\text{Fe}_2\text{CoO}_4$

For the sake of comparison, the behaviour of a suspension of colloidal  $\text{Fe}_2\text{CoO}_4$  was investigated in the same conditions as  $\text{Fe}_3\text{O}_4$  ( $\text{Fe}_2\text{CoO}_4$  is an inverse spinel too).

Titrating the suspension in the presence of  $\text{HClO}_4$  or of  $\text{Fe}(\text{NO}_3)_3$  gave features similar to those observed with  $\text{Fe}_3\text{O}_4$ : neutralization of free acidity or of excess FeIII ending at pH 4-5, followed by the precipitation of  $\text{Co}(\text{OH})_2$  ending at pH 8-9. In every case, only CoII ions were desorbed, and no significant Fe was released into solution.

The stoichiometry of the "exchange" in acidic medium was still equal to 2 ( $|\text{H}^+|_c / |\text{CoII}|_R = 2$ ). CoII desorption from  $\text{Fe}_2\text{CoO}_4$ ,

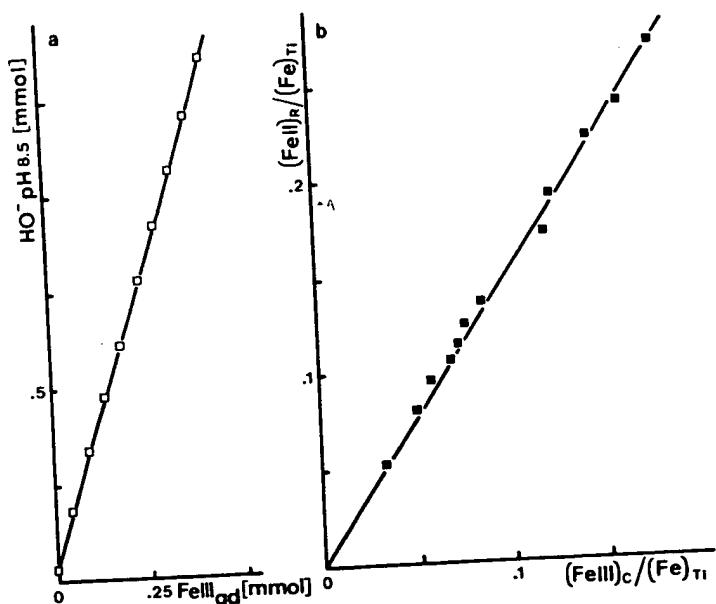


FIG. 5. Exploitation of titration of mixtures of  $\text{Fe}_3\text{O}_4 + \text{Fe}(\text{NO}_3)_3$ .  $0.64 \times 10^{-3}$  mole  $\text{Fe}_3\text{O}_4$ ;  $0 \leq |\text{FeIII}|_{ad} / |\text{Fe}|_{ini} \leq 0.21$ . (a) Amount of base added at pH 8.6 vs amount of FeII initially added ( $|\text{FeII}|_{ad}$ ). (b) Amount of released FeII ( $|\text{FeII}|_R$ ) vs amount of consumed FeIII (not titratable at pH 4.5) ( $|\text{FeIII}|_c$ ). Amounts relative to total Fe initially in  $\text{Fe}_3\text{O}_4$  ( $|\text{Fe}|_T$ ).

however, proved much limited compared to FeII desorption from  $\text{Fe}_3\text{O}_4$ : ca. 10% of the Co amount was actually released, for a starting mixture corresponding to  $|\text{H}^+|/|\text{Co}| = 4$ . In the presence of  $\text{Fe}(\text{NO}_3)_3$ , the process was limited also. The reaction stoichiometry differed from the  $\text{Fe}_3\text{O}_4$  case: the ratio  $|\text{CoII}|_R/|\text{FeIII}|_C$  was in the range 1–1.3, compared to 1.5 ( $|\text{FeII}|_R/|\text{FeIII}|_C$ ) for  $\text{Fe}_3\text{O}_4$  (experimental error may, however, be significant owing to the small quantities involved in assessing the stoichiometry).

## 2. STRUCTURAL STUDY

Four samples were investigated: colloidal  $\text{Fe}_3\text{O}_4$  freshly prepared (M), treated with  $\text{HClO}_4$  (H), treated with  $\text{Fe}(\text{NO}_3)_3$  (Fe), and dried under reduced pressure and aged in air at room temperature for a month (O). Compositions ( $|\text{FeII}|/|\text{FeIII}|$ ) are given in Table I.

### 2.1. X-Ray Diffraction

Only the lines typical of the spinel structure were detected in each case. Values of the unit cell parameter were 8.40 Å (M) and 8.35–8.36 Å (O, H, Fe).

Investigation of the line widths ( $X$ ) indicated two types of material. The plot  $X \cos \theta$  vs  $\sin \theta$

(Fig. 6) yields a horizontal line that is identical for samples (M), (O), and (H). Line broadening is therefore attributed to particle size effect (24). By applying the Scherrer formula, a common apparent size of  $D_x = 95 \text{ \AA}$  is deduced. This is consistent with microscopy data (Table I) given the variation in the averaging process. For sample (Fe), on the other hand, the data  $X \cos \theta$  vs  $\sin \theta$  are much scattered. No significant line shift, line asymmetry, or background anomaly was observed in the pattern. A second phase, disordered and independent of the spinel one from the diffraction standpoint, therefore seemed unlikely. With morphological features being ruled out by microscopy observations, the anisotropic line broadening is attributed to important disordering in the spinel particle.

Quantitative studies of integrated intensities for materials oxidized (20) or treated in acidic medium (14) have already been reported. The structures were found to be quite similar, with little variation in the Fe atom distribution. This distribution appeared more random than usually admitted: apart from octahedral vacancies (equipoint position 16d in  $Fd\bar{3}m$ ), a significant fraction of tetrahedral vacancies (8a) was involved along with noticeable occupation of interstitial tetrahedral sites (48f). Intensities obtained for samples (O) and (H)

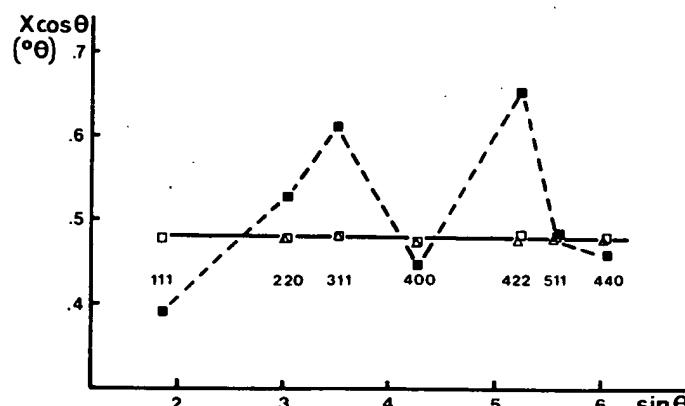


FIG. 6. Variation of the X-ray diffraction line broadening for colloidal  $\text{Fe}_3\text{O}_4$ , freshly prepared ( $\Delta$ ),  $\text{HClO}_4$ -treated ( $\square$ ), and  $\text{Fe}(\text{NO}_3)_3$ -treated ( $\blacksquare$ ). Data for  $\text{Fe}_3\text{O}_4$  oxidized in air are indistinguishable from ( $\square$ ) and are not given for the sake of clarity.

TABLE II  
Intensity of Observed X-Ray Diffraction Lines in  $\text{H}^+$ - and FeII-Treated Magnetite

Sample	$hkl$						
	111	220	311	400	422	511	440
H	10	140	650	245	120	505	1000
Fe	10	90	545	230	60	400	1000

proved consistent with such results. Significant deviations were observed for sample (Fe). By scaling with the 440 line intensity, practically all intensities (Table II), except that of line 400, are lowered. Atoms within a given set of equivalent sites (anionic 32e, cationic tetrahedral 8a, 8b, 48f, octahedral 16d, 16c) scatter in phase for reflections 400 and 440, and oxygen atom contribution to other lines is small. This, along with unbroadening of lines 400 and 440 (Fig. 6), suggests that increasing disorder of the cation stacking may be the main feature. Structure factor calculations suggest that coherent twinning may be involved.

## 2.2. Mössbauer Effect

Mössbauer spectra of samples (M, O, H, Fe) are shown in Fig. 7. Spectrum (M) is typical of magnetite particles about 100 Å in size (25). It is mainly based on the two six-line patterns of bulk  $\text{Fe}_3\text{O}_4$ , one for FeIII ions in sites A and the other for FeII and FeIII ions in sites B (labelled 1 and 2, respectively). FeII and FeIII ions of type B are not differentiated at room temperature owing to electron hopping that is faster than the measurement characteristic time ( $10^{-10}$  sec against  $10^{-8}$  sec, roughly). They exhibit an average valence of 2.5. In partly oxidized materials, an unpaired FeIII ion gives the same contribution as a FeII ion of type A (16). Because of small FeII content, the relative intensity of component 2 is much decreased in spectra (O, H, Fe) and it is responsible for the overall residual asymmetry. All patterns exhibit asymmetric line broadening, reflecting the presence of hyperfine field ( $H_f$ ) distributions.

$H_f$  distributions were computed using a constrained least-squares method (26). Characteristics of the fits are summarized in Table III. Values of the isomer shift, and of the highest field involved ( $H_0$ ), are consistent with those of bulk  $\text{Fe}_3\text{O}_4$  (sample M) and of bulk  $\gamma\text{Fe}_2\text{O}_3$  with a few pairs of FeII-FeIII persisting (samples O, H, Fe). Data for the component area ratio agree very well with chemical analysis results (Table I).

$H_f$  distributions for FeIII ions in samples (O, H, Fe) are shown in Fig. 8. The observed

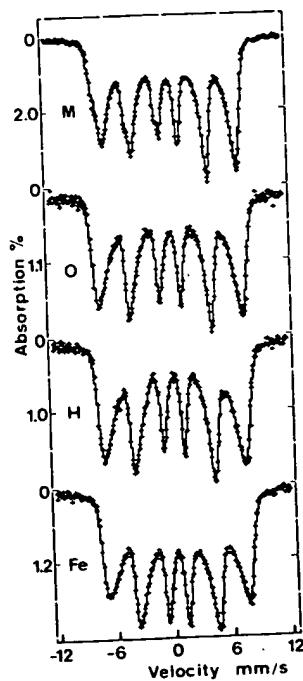


FIG. 7. Mössbauer spectra (300 K) of colloidal  $\text{Fe}_3\text{O}_4$ , freshly prepared (M), oxidized in air (O),  $\text{HClO}_4$ -treated (H), and  $\text{Fe}(\text{NO}_3)_3$ -treated (Fe).

TABLE III  
Hyperfine Parameters of the Samples

Sample	Site	$\bar{H}$ (kOe)	$\sigma$ (kOe)	$H_m$ (kOe)	$p_c$	$S$
M	1			450		
	2	340	110	425	0.18	1.70
O	1	391	109	466	0.12	0.13
	2			420		
H	1	397	90	453	0.07	0.14
	2			425		
Fe	1	351	119	453	0.20	0.09
	2			425		

Note. Fixed parameters: Isomer shift (relative to the source): 1, 0.16 mm/sec (M) and 0.22 mm/sec (O, H, Fe); 2, 0.60 mm/sec (M, O, H, Fe). Quadrupole splitting is neglected. Elementary sextuplet (3:2:1:1:2:3) of Lorentzian lines with full width at half maximum: 1, 0.40 mm/sec (M) and 0.55 mm/sec (O, H, Fe); 2, 0.60 mm/sec (M, O, H, Fe).  $H_f$  distributions are computed using 40 steps for the major component and 14 steps for the other one.  $\bar{H}$  is the mean hyperfine field,  $\sigma$  is the standard deviation,  $H_m$  is the hyperfine field at maximum, and  $p_c$  is the cumulative fraction at 240 kOe. Highest field involved ( $H_0$ ): 1, ~505 kOe (M) and 507 kOe (O, H, Fe); 2, 470 kOe (M) and ~455 kOe (O, H, Fe).  $S$  is the ratio of component area 2/1 (assuming identical recoilless fractions,  $|FeII|/|FeIII| = S/(S + 2)$ ).

oscillations may be due to the fact that identical parameters were taken for the two kinds of ion (A, B unpaired). Nevertheless it is clear that the hyperfine field is spread over the range 500–50 kOe approximately, in the three cases. Distributions in samples (O) and (H) mainly differ in the value of the field at maximum ( $H_m$ ), lowered by 10 kOe roughly in sample (H). The value of  $H_m$  in sample (Fe) is the same as in sample (H), but the distribution is markedly broadened. No nonmagnetic component is detected.

#### DISCUSSION

Structural results show that, similarly to aerial oxidation, treatment with  $HClO_4$  (pH 2–2.5) or with  $Fe(NO_3)_3$  makes the  $Fe_3O_4$  particles basically retain the spinel structure and transform to  $\gamma Fe_2O_3$ -like particles, without significant alteration of the particle size. Out-

standing features are widely spread hyperfine field distributions and marked disordering induced by the treatment with  $Fe(NO_3)_3$ .

The observed  $H_f$  distributions, which involve hyperfine fields reduced by ca. 80–90% with respect to the bulk value, cannot be explained on the basis of the classical magnetic behaviour of small homogeneous noninteracting particles (25). It suggests that surface effects (27) and/or magnetic interparticle (MIP) interactions (28) may be operative. The  $H_f$  variation with respect to the bulk is usually small at a surface site. In  $\gamma Fe_2O_3$  acicular particles (29, 30) the reduction does not exceed 15% at room temperature. Surface effects may, however, be enhanced if surface structural modifications or chemisorption phenomena occur. Magnetic coupling of the particles can actually yield very broad  $H_f$  distributions, from  $H_0$  down to zero, provided the interaction anisotropy is predominant over the other anisotropies (28, 31), and in the appropriate range. MIP interactions may be of the dipole or exchange type. The latter can occur between faceted spins at the surface of adjacent particles, and they are short-ranged and strongly depen-

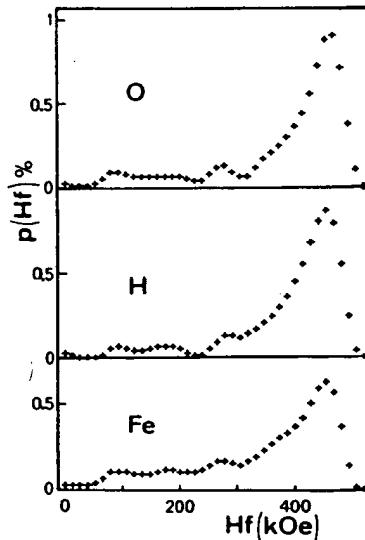


FIG. 8. Hyperfine field distribution for FeIII in colloidal  $Fe_3O_4$  oxidized in air (O),  $HClO_4$ -treated (H), and  $Fe(NO_3)_3$ -treated (Fe).

ent upon the surface state. MIP interactions between the aggregates (chains or coils) that constitute the stable sols (32) are likely mainly of the dipole type. Exchange coupling, on the other hand, is likely predominant in sols flocculated by surface charge cancelling, or even by electrolyte effect (22). A similar situation is believed to occur in materials of concern here.

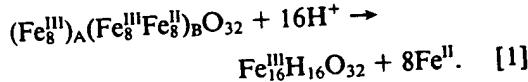
Surface effects and particle coupling combine. They can hardly be characterized separately. Assuming the materials to be similarly dried, we can reasonably consider that  $H_f$  distribution spreading towards lower fields reflects decreasing particle coupling owing to increasing surface perturbation.

X-ray diffraction and Mössbauer spectroscopy observations therefore consistently allow one to deduce that the particle structure is basically the same in the three cases, namely,  $\gamma\text{Fe}_2\text{O}_3$ -like, and that treating  $\text{Fe}_3\text{O}_4$  particles with  $\text{HClO}_4$  induces a weak perturbation of the surface state compared to aerial oxidation, but that the treatment with  $\text{Fe}(\text{NO}_3)_3$  causes important structural disordering at the particle surface.

#### MAGNETITE IN ACIDIC MEDIUM

In acidic medium, near pH 2–2.5, colloidal magnetite releases iron, in the FeII state exclusively, while protons are consumed in solution. All FeII can thus be released.

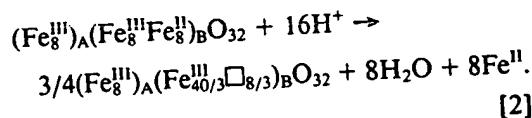
The reaction stoichiometry ( $2\text{H}^+$ /FeII) cannot correspond to a simple ionic exchange between the solid and the solution with ions of both types interdiffusing, for it would produce an oxihydroxide  $\text{FeOOH}$  according to



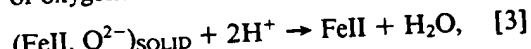
That seems quite unlikely given the structural results, even if the question of hydrogen in the materials  $\gamma\text{Fe}_2\text{O}_3$ - $\text{Fe}_3\text{O}_4$  remains open (16, 19).

Owing to pH conditions, incompatible with spinel oxide formation and to reaction rate,

we may discard a dissolution-precipitation mechanism and, consistent with the structural features, we may write



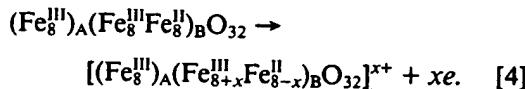
FeII is then removed with an equal amount of oxygen:



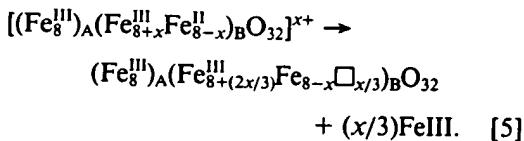
which corresponds to solubilisation of lattice FeII. Surface hydration or hydroxylation likely occurs, more or less deeply (33), so that Eq. [2] indeed represents an ideal limit.

Since the particle size does not change noticeably, and the structure is not altered significantly, reaction [3] likely develops on a limited depth. If it provokes the particle dissolution, it must be followed by fast readsorption of hydroxylated FeIII species (FeIII is much more hydroxylated than FeII) since FeIII is never detected in solution. Such a process seems unlikely, given the medium acidity conditions. Furthermore, since no disordering is observed, it assumes that FeIII is readsorbed in the right sites of the spinel lattice, which looks quite unrealistic (see below). We therefore conclude that surface FeII is selectively leached.

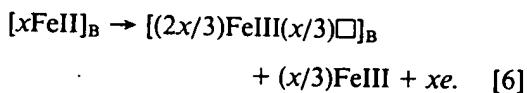
The first kinetic step of the reaction, which is quasi-instantaneous, corresponds to release of 40% of the total FeII content. Assuming FeII is homogeneously distributed within the  $\text{Fe}_3\text{O}_4$  particle, it corresponds to complete removal of octahedral Fe from an outermost layer, roughly 4 Å thick (ca. half a unit cell thick). The equivalent amount of oxygen simultaneously removed approximately represents a 60% loss for the first surface oxygen layer (2.8 Å). Then, the particle periphery practically contains FeIII only. Further FeII desorption requires the reduction of the new surface FeIII. It implies an electron supply from the interior and, therefore, a partial oxidation of  $\text{Fe}_3\text{O}_4$ . Let  $x$  be the number of transferred electrons, then we may have



In order to keep the charge balance, excess cations have to migrate (as FeII or, more likely, as FeIII + e), leaving vacancies in the octahedral sublattice according to



The net stoichiometry of FeII oxidation is



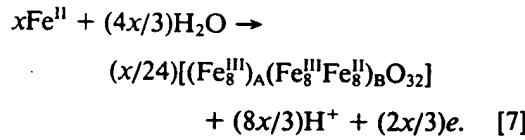
Excess FeIII arriving at the surface is then reduced and released in turn with the equivalent amount of oxygen as H<sub>2</sub>O (Eq. [3]). At the limit (x = 8), we have a γ-Fe<sub>2</sub>O<sub>3</sub> particle, and the net reaction stoichiometry is given by Eq. [2].

Cation diffusion likely occurs step by step. Given an octahedral cation, the nearest vacant sites are the interstitial tetrahedral sites (48f) mentioned earlier. They may offer an easy pathway. Significant occupation of these sites in the room temperature disordered phase γ-Fe<sub>2</sub>O<sub>3</sub> may thus be related to the oxidation process, with too low an activation energy to completely remove the defects. Cation migration probably controls the reaction rate since electron transfer is very fast (21) and the FeII ions formed by reduction in the surface are in a highly reactive state (1, 34). The rate is also influenced by the decreasing number of pairs FeII-FeIII during the process.

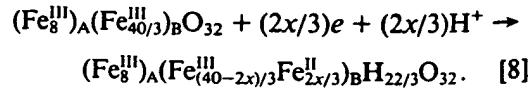
The behaviour of Fe<sub>2</sub>CoO<sub>4</sub> in the same conditions supports the proposed mechanism. CoII ions occupy the same sites as FeII in Fe<sub>3</sub>O<sub>4</sub>. In solution, CoII and FeII exhibit similar characteristics towards hydrolysis (35). If hydrolysis were the reaction-determining step, both types of colloid would behave similarly. The observed release of CoII roughly corresponds to the amount of CoII contained in the first monolayer. The very limited desorption

of CoII compared to FeII must be related to lack of electron delocalization in Fe<sub>2</sub>CoO<sub>4</sub> (36). If electron transfer had been involved, however, in the reduction of surface ions, FeII would have likely been released too, which was not observed.

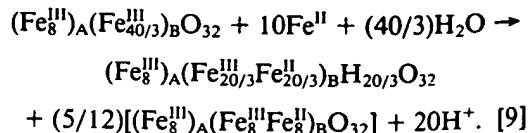
Once all FeII is removed from the Fe<sub>3</sub>O<sub>4</sub> particle in acidic medium, it can be readsorbed by rising the pH from 2 to 5 or 6 (14). Two protons are freed in solution per FeII ion adsorbed. FeII uptake stops when the overall composition is |FeII|/|FeIII| ~ 0.5. Acidity conditions and reaction rate allow one to discard a dissolution-precipitation process, in contrast to the transformation γ-FeOOH → Fe<sub>3</sub>O<sub>4</sub> by adsorption of FeII (37). It was suggested that the reaction is assisted by electron transfer, this time directed from the surface towards the core. It was shown that there is an ordered extension of the colloid with a growing Fe<sub>3</sub>O<sub>4</sub>-like layer (~5 Å thick), and likely reduction of octahedral FeIII in the interior. A schematic process may be outlined as follows: because of easy electron delocalization on B sites, FeII ions adsorbed under species like Fe<sup>II</sup>(OH)<sub>a</sub>(OH<sub>2</sub>)<sub>6-a</sub><sup>(2-a)+</sup> build up an epitaxial Fe<sub>3</sub>O<sub>4</sub> layer, which may be summarized by



Electrons are pumped in by underlying octahedral FeIII ions, the charge balance is preserved by inwards diffusion of protons, and we have in the core



The reaction stops when there are as many FeII as FeIII ions on sublattice B, that is, for x = 10. The net reaction stoichiometry then is



corresponds to formulae  $\text{Fe}_{5.53}\text{H}_{1.18}\text{O}_8$  and  $\text{H}_{1.67}\text{O}_8$  for the whole particle and the  $\text{O}_{12}$ , respectively.

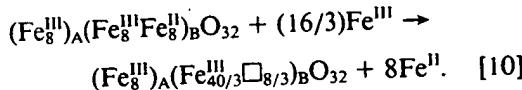
Desorption and adsorption of FeII are not symmetric, but they may be viewed as "reversible" phenomena as far as electron transfer in either direction is involved.

Colloidal spinel iron oxide strikingly stands out from other colloidal oxides regarding adsorption and surface precipitation phenomena. Its peculiar behaviour results from easy electron delocalization, from few structural changes between reduced ( $\text{Fe}_3\text{O}_4$ ) and oxidized ( $\gamma\text{Fe}_2\text{O}_3$ ) forms, and from adequate particle size which allows the electron reservoir, which the colloid is, to empty and refill in a reasonable time. It considerably enhances acid-base phenomena in the interface.

#### BEHAVIOUR IN FeIII MEDIUM

In the presence of FeIII in solution, colloidal magnetite exhibits a behaviour similar to that observed in  $\text{HClO}_4$  medium: FeII appears in solution while FeIII is consumed. All FeII can be released.

The reaction stoichiometry ( $|\text{FeII}|_R / |\text{FeIII}|_C = 1.5$ ) may be written



It preserves the charge balance in the lattice, but direct interchange in sublattice B is quite unrealistic.

Once more, reduction in surface, supplied with electrons by magnetite oxidation in the inner layer (Eq. [5]), is most likely to occur. The net stoichiometry (Eq. [10]) implies a net release of FeII from the colloid. Two extreme situations may occur:

- (i) all adsorbed FeIII is reduced and released ((16/3)FeII) along with reduced excess cations ((8/3)FeII) or
- (ii) no adsorbed FeIII is reduced, only FeIII from the lattice is reduced and released (8FeII).

The important structural disordering induced by treatment with  $\text{Fe}(\text{NO}_3)_3$  compared to  $\text{HClO}_4$  goes against the first assumption and supports effective adsorption of FeIII from solution. The adsorbate structure, though disordered, is not completely at random as testified by the lack of nonmagnetic component in the hyperfine field distribution, and by index-dependent broadening of the spinel diffraction lines.

Given the medium acidity conditions, FeIII in solution is under variously hydroxylated forms such as  $\text{Fe}(\text{OH})(\text{OH}_2)_5^{2+}$ ,  $\text{Fe}(\text{OH})_2(\text{OH}_2)_4^+$ , or  $\text{Fe}_2(\text{OH})_2(\text{OH}_2)_8^{2+}$  (35). Since the pH is nearly the same as with  $\text{HClO}_4$ , we may reasonably consider that the reaction is initiated by rapid protolysis in the particle surface, resulting in FeII release. Simultaneously, FeIII species may be adsorbed onto the surface, organizing themselves more or less orderly on available sites, thus bringing enough supply of protons to keep FeII leaching going. Within the particle, the various tetrahedral or octahedral sites are not equivalent. This is less obvious in the surface, and stacking faults are therefore likely to occur. Electron supply from the interior proceeds via hopping between Fe ions on a definite sublattice. In the interface, adsorbent FeIII may therefore be reduced preferentially to adsorbate FeIII.

The results concerning  $\text{Fe}_2\text{CoO}_4$  emphasize again the role of FeII-FeIII electron transfer. Colloid desorption is very limited. The reaction stoichiometry ( $|\text{CoII}|_R / |\text{FeIII}|_C$  in the range 1–1.3) shows that FeIII uptake is rather small, and that release of CoII is more likely due to degradation of the particle surface owing to the medium acidity.

#### COLLOID PEPTIZATION

$\text{Fe}_3\text{O}_4$  particles are not peptized in acidic medium unless a certain level of FeII desorption has been reached. It clearly shows that the development of substantial electrical surface charge requires that the surface layer be porous enough. Porosity results from:

(i) Surface hydrolysis which tends preferentially to empty octahedral sites, increasing the surface roughness and the number of surface oxygen atoms to be protonated (iron in tetrahedral sites is probably reduced too in the surface, but less easily (3)).

(ii) Cation vacancies which, at least in surface, may help protons to diffuse. The role of vacancies is also corroborated by the fact that aerial oxidation is necessary for magnetite to give sols in alkaline medium (13).

Peptization in FeIII medium is probably helped by the poorly ordered structure of the adsorbate layer. It likely enables the diffusion of protons, thus increasing the number of charged sites.

#### CONCLUSION

We have shown that  $\text{Fe}_3\text{O}_4$  can be transformed into  $\gamma\text{Fe}_2\text{O}_3$  without an oxidizing agent. It likely involves electron trapping in octahedral surface sites. We suggest that protonation of surface OH groups perturbs the electron density in the metal-oxygen bonding ( $\text{M} \rightarrow \text{OH}_2^+$ ), which an octahedral cation, normally paired by electron hopping, can balance: it traps the electron, its valence drops from 2.5 to 2, and it becomes highly reactive and breaks its bonding with the lattice easily. Its partner therefore experiences an electron loss which it tends to recover from the next pair. Step by step, the whole sublattice gets disturbed. Charge imbalance is locally compensated by outwards migration of excess cations which renew the surface, are reduced, and released in turn.

The mechanism is somewhat similar to that of aerial oxidation (15). There, surface FeII ions ionize adsorbed oxygen which they coordinate themselves to, building up a new oxide layer. As the presence of water seems necessary to magnetite aerial oxidation (18), we suggest it may be catalyzed by surface hydration. Oxidation in neutral or alkaline medium likely parallels the "dry" aerial oxidation: surface FeII ions oxidize and coordinate them-

selves to oxygen, this being induced by adsorption of oxygenated species from solution.

The various situations look relevant to the same electronic process: electron transfer through the interface relayed by electron transfer within the particle. The intrinsic structural mechanism is likely the same, but the adsorption phenomena that induce the reaction and the outward conditions that rule the behaviour of surface FeII are, however, distinct. Changes in adsorption equilibria, or more generally in the particle surroundings, are therefore expected to result in important kinetic effects, as is observed (19).

Generally, when considering adsorption/desorption of potential determining ions ( $\text{H}^+$ ,  $\text{HO}^-$ ), processes which induce the surface electric charge are restricted to the oxide surface in contact with electrolyte (38, 39). In many cases such phenomena are quantitatively explained using elaborate models, taking account of specific adsorption of ionic species present in the medium (40, 41). The interface is then considered as polarizable, and charged species are transferred between surface plane and bulk solution. Such a framework is adapted to the behaviour of large  $\text{Fe}_3\text{O}_4$  particles at  $\text{pH} \geq 4$  (9, 10). It is no longer consistent for the small particles of concern here. The interface is better described by gel models (33, 42, 43) that involve an interface layer more or less deep, which adsorbed ions may diffuse in.

Moreover, the interface reversibility (44) has to be taken into account: in addition to reactions of proton adsorption/desorption, a reversible transfer of ions of the solid (metal, oxygen), which may not be stoichiometric, also contributes to the surface charge. Measurements of the total particle charge reported here do not enable one to separate both types of contribution since the stoichiometric relations are established by acid-base neutralization of the suspension. Nevertheless, these two reactions are qualitatively differentiated unambiguously. For many oxides, the contribution of lattice ions to the surface charge is very low

and not considered. It cannot be so in the case of colloidal  $\text{Fe}_3\text{O}_4$  since acid-base reactions in the interface are closely related to electron delocalization within the solid.

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